

Crystallization of Simple Fluids: Relative Stability of f.c.c. and b.c.c Structures

Swarn Lata Singh and Yashwant Singh

Department of Physics, Banaras Hindu University, Varanasi-221 005, India

(Dated: February 27, 2009)

Abstract

A free-energy functional for a crystal that contains both the symmetry conserved and symmetry broken parts of the direct pair correlation function is developed. The free-energy functional is used to investigate the crystallization of fluids interacting via the inverse power potential ; $u(r) = \epsilon(\sigma/r)^n$. In agreement with simulation results we find that for $n = 12$ the freezing is into close packed f.c.c structure while for soft repulsions ($n \leq 6$) b.c.c phase is more stable.

PACS numbers: 64.70.dg, 64.70.dm, 05.70.Fh

When a fluid freezes into a crystalline solid its continuous symmetry of translation and rotation is broken into one of the symmetry groups of the Bravais lattices. A crystalline solid has a discrete set of vectors \mathbf{R}_i such that any function of position, such as one particle density satisfies $\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R}_i)$ for all \mathbf{R}_i [1]. This set of vectors necessarily forms a Bravais lattice. While many metallic systems freeze into b.c.c structure, simple fluids like Ar freeze into f.c.c structure [2]. Model fluids interacting via inverse power potentials $u(r) = \epsilon(\sigma/r)^n$ where ϵ , σ and n are potential parameters and r molecular separation, show interesting freezing transitions [3-5]. The more repulsive ($n \geq 7$) systems freeze into f.c.c structure while the soft repulsions $n \leq 6$ freeze into b.c.c phase. A correct description of the stability of the two cubic structures is a stringent test of any statistical mechanical theory based on first principle, since atomic arrangements in the two are very different.

Since 1979 [6] the density functional theory (DFT) has been applied to the problem of crystallization of a wide variety of fluids [7-8]. Despite its many successes notably with hard sphere system, a full theory applicable to all intermolecular potentials has remained elusive [7-11]. The direct pair correlation function (DPCF) that appears in the expression of the free-energy functional corresponds to the ordered phase and is functional of $\rho(\mathbf{r})$. When this DPCF is replaced by that of the co-existing isotropic liquid [6] or by that of an “effective fluid” [12], the free-energy functional becomes approximate and fails to provide a correct description of the freezing transition. Attempts to include a term involving three-body direct correlation function of the isotropic phase in the free-energy functional have failed to improve the situation [9,10].

Due to breaking of symmetry at the fluid-solid transition a qualitatively new contribution [13,14] to the pair correlation function of a crystal arises. The pair correlation function of a crystal has therefore two different contributions; one that maintains the continuous symmetry of the Hamiltonian and passes smoothly through the transition and the other that breaks it and vanishes at the melting point. In this Letter we develop a method to estimate the DPCF of a crystal and use it to construct a free energy functional by performing functional integrations in the appropriate domains of density space. We use this free-energy functional to investigate the crystallization of fluids interacting via the inverse power potential. Potentials of this class have a simple scaling property according to which the reduced excess thermodynamic properties depend on a single variable which is defined as $\gamma = (\rho\sigma^3)(\epsilon/k_b T)^{(3/n)} = \rho^* T^{*(-3/n)}$ where k_b is the Boltzmann constant and

T, temperature. The equation of state and the melting curve of these potentials have been extensively investigated by Monte Carlo (MC) simulations for several values of parameter n so that “exact” results are available [3-5] for comparison.

The reduced free-energy $A[\rho]$ of an inhomogeneous system is functional of $\rho(\mathbf{r})$ and is written as $A[\rho] = A_{id}[\rho] + A_{ex}[\rho]$ where $A_{id} = \int d\mathbf{r} \rho(\mathbf{r}) [\ln(\rho(\mathbf{r})\Lambda) - 1]$ is the ideal gas part. Here Λ is the cube of thermal wavelength associated with a particle. The excess part $A_{ex}[\rho]$ is related with the DPCF of the system as [14]

$$\frac{\delta^2 A_{ex}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} = -c^{(0)}(r, \rho_0) - c^{(b)}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) \quad (1)$$

where $c^{(0)}$ is symmetry conserving and $c^{(b)}$ symmetry broken parts of the DPCF. While $c^{(0)}$ depends on the magnitude of the interparticle separation and is function of the average number density ρ_0 , $c^{(b)}$ is invariant only under discrete set of translations and is functional of $\rho(\mathbf{r})$. If one chooses a center of mass variable $\mathbf{r}_c = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and difference variable $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, then $c^{(b)}$ can be written as [15];

$$c^{(b)}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = \sum_{\mathbf{G}} \exp i(\mathbf{G} \cdot \mathbf{r}_c) c^{(G)}(\mathbf{r}; [\rho]) \quad (2)$$

where \mathbf{G} are reciprocal lattice vectors (R. L. V.). Since the DPCF is real and symmetric with respect to interchange of \mathbf{r}_1 and \mathbf{r}_2 , $c^{(G)}(\mathbf{r}) = c^{(-G)}(\mathbf{r})$ and $c^{(G)}(\mathbf{r}) = c^{(G)}(-\mathbf{r})$

The Ornstein-Zernike equation and the Roger-Young closure relation [16] have been used to calculate $c^{(0)}(r)$ and $\frac{\partial c^{(0)}(r)}{\partial \rho}$ as a function of intermolecular separation for densities ranging from zero to a density above the melting point at small intervals for $n=12, 6$ and 4 . This method gives values of pair correlation functions which are thermodynamically self consistent. For $c^{(b)}(\mathbf{r}_1, \mathbf{r}_2, [\rho])$ one can either generalize the integral equation method [14] or use a functional Taylor expansion [7]. In the latter the contribution due to inhomogeneity to the DPCF is obtained from the higher-order direct correlation functions of the isotropic phase. The leading term of this expansion gives

$$c^{(b)}(\mathbf{r}_1, \mathbf{r}_2; [\rho]) = \int c_3^{(0)}(r_{12}, r_{13}, r_{23}; \rho_0) (\rho(\mathbf{r}_3) - \rho_0) d\mathbf{r}_3 \quad (3)$$

where $\rho(\mathbf{r}_3) = \rho_0 + \rho_b(\mathbf{r}_3)$ with $\rho_b(\mathbf{r}_3) = \rho_0 \sum_{\mathbf{G} \neq 0} \mu_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}_3)$ and $c_3^{(0)}$ is the three-body DPCF of the isotropic fluid of density ρ_0 , $\mu_{\mathbf{G}}$ are order parameters and the sum is over the complete set of R.L.V of the crystal. Eq.(3) satisfies the condition that $c^{(b)}$ is zero in the isotropic phase and depends on the amplitude and phase factors of density waves which arise

in a crystal due to breaking of symmetry of fluid. Though the higher order terms in (3), particularly for softer spheres, are not negligible and will affect the location of fluid-solid transition [17], the relative stability of the two cubic structures can however be understood on the basis of (3) as the error caused due to neglect of higher order terms in both structures are of similar magnitude.

Barrat et.al [9] have shown that $c_3^{(0)}$ can be factorized as $c_3^{(0)}(r_{12}, r_{13}, r_{23}) = t(r_{12})t(r_{13})t(r_{23})$ and the function $t(r)$ can be determined from the relation

$$\frac{\delta c^{(0)}(r)}{\delta \rho} = t(r) \int t(r_{13})t(r_{23})d\mathbf{r}_3 \quad (4)$$

Using above relations we find the following relation for $c^{(G)}(\mathbf{r})$:

$$c^{(G)}(\mathbf{r}) = \sum_{lm} \left[\frac{\rho_0 \mu_G}{2\pi^2} \sum_{l_1} \sum_{l_2} i^{(l_1+l_2)} (-1)^{l_2} \frac{(2l_1+1)(2l_2+1)}{(2l+1)} (C_g(l_1 l_2 l; 000))^2 \right. \\ \left. j_{l_2}(\frac{1}{2}Gr) t(r) B_{l_1}(r, G) Y_{lm}^*(\hat{\mathbf{G}}) \right] Y_{lm}(\hat{\mathbf{r}}) \quad (5)$$

where C_g is the Clebsch-Gordan coefficient, $j_l(x)$ the spherical Bessel function and

$$B_{l_1}(r, G) = (4\pi)^2 \int dk k^2 t(k) j_{l_1}(kr) \int dr' r'^2 t(r') j_{l_1}(kr') j_{l_1}(Gr') \quad (6)$$

The crystal symmetry dictates that l and l_1+l_2 are even and for a cubic crystal, $m = 0, \pm 4$. If we write $c^{(\mathbf{G})}(\mathbf{r}) = \sum_{lm} c_{lm}^{(G)}(r) Y_{lm}(\hat{\mathbf{r}})$, the expression given in the square bracket in (5) is the expression for $c_{lm}^{(G)}(r)$. The $c_{lm}^{(G)}(r)$ depends on the order parameter and on the magnitude of R.L.V.

In Figs. 1 and 2 we compare few harmonic coefficients $c_{lm}^{(G)}(r)$ of the DPCF of f.c.c and b.c.c structures for $n=12$ for R.L.V of first and second sets, respectively. We note that the values of $c_{lm}^{(G)}(r)$ are far from negligible and differ considerably for the two structures; the difference is both in magnitude and in r dependence. It is this difference that plays crucial role in giving relative stability to one crystalline structure over the other. As the magnitude of \mathbf{G} increases the values of $c_{lm}^{(G)}(r)$ decreases and after the ninth set of R.L.V values become negligible.

The functional integration of (1) in density space gives $A_{ex}[\rho]$. In this integration the system is taken from some initial density to the final density $\rho(\mathbf{r})$ along a path in the density space; the result is independent of the path of integration [18]. Since the symmetry

conserving part $c^{(0)}$ depends on number density only, the integration is done taking the density of the coexisting fluid ρ_l as reference. This leads to

$$A_{ex}^{(0)}[\rho] = A_{ex}(\rho_l) - \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \Delta\rho(\mathbf{r}_1) \Delta\rho(\mathbf{r}_2) \bar{c}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \quad (7)$$

where $\bar{c}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = 2 \int_0^1 d\lambda \int_0^1 d\lambda' c^{(0)}(r; \rho_l + \lambda\lambda'(\rho_0 - \rho_l))$, $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_l$, $A_{ex}(\rho_l)$ is the excess reduced free energy of the isotropic fluid of density ρ_l and $\rho_0 = \rho_l(1 + \Delta\rho^*)$ is the average density of the ordered phase. Since the functional integrations of $c^{(b)}$ have to be done in the density space specified by the order parameter μ_G and the number density ρ_0 we define the path of integration by two parameters λ and ξ which vary from 0 to 1. The parameter λ raises the density from 0 to ρ_0 as it varies from 0 to 1 whereas parameter ξ raises the order parameter from 0 to μ_G as it varies from 0 to 1. This integration gives

$$A_{ex}^{(b)} = -\frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho_b(\mathbf{r}_1) \rho_b(\mathbf{r}_2) \bar{c}^{(b)}(\mathbf{r}_1, \mathbf{r}_2) \quad (8)$$

where

$$\bar{c}^{(b)}(\mathbf{r}_1, \mathbf{r}_2) = 4 \int_0^1 d\xi \xi \int_0^1 d\xi' \int_0^1 d\lambda \lambda \int_0^1 d\lambda' c^{(b)}(\mathbf{r}_1, \mathbf{r}_2; \lambda\lambda'\rho_0; \xi\xi'\mu_G) \quad (9)$$

The free energy functional for a crystal is the sum of A_{id} , $A_{ex}^{(0)}$ and $A_{ex}^{(b)}$.

The grand thermodynamic potential defined as $-W = A - \beta\mu \int d\mathbf{r} \rho(\mathbf{r})$, where μ is the chemical potential, is used to locate transition as it ensures that the pressure and chemical potential of two phases remain equal at the transition. The transition point is determined by the condition $\Delta W = W_l - W = 0$ where W_l is the grand thermodynamic potential of the fluid. We calculate the ideal gas part of ΔW using the Gaussian ansatz [19] for the solid density $\rho(\mathbf{r}) = (\alpha/\pi)^{3/2} \sum_{\mathbf{R}_i} \exp(-\alpha(\mathbf{r} - \mathbf{R}_i)^2)$, α being the localization parameter and for the excess part the Fourier form with $\mu_G = \exp(-G^2/4\alpha)$.

$$\begin{aligned} \frac{\Delta W}{N} = 1 - (1 + \Delta\rho^*) \left[\frac{5}{2} + \ln \rho_l - \frac{3}{2} \ln(\alpha/\pi) \right] - \frac{1}{2} \Delta\rho^{*2} \hat{c}^{(0)}(0) - \frac{1}{2} \sum_{\mathbf{G} \neq 0} |\mu_G|^2 \hat{c}^{(0)}(G) \\ - \frac{1}{2} \sum_{\mathbf{G}} \sum_{\mathbf{G}_1} \mu_{G_1} \mu_{-G-G_1} \hat{c}^{(G)}(\mathbf{G}_1 + \frac{1}{2}\mathbf{G}) \end{aligned} \quad (10)$$

where $\hat{c}^{(0)}(G) = \rho_l \int c^{(0)}(r) e^{i\mathbf{G} \cdot \mathbf{r}} d\mathbf{r}$ and $\hat{c}^{(G)}(\mathbf{G}_1 + \frac{1}{2}\mathbf{G}) = \rho_l \sum_{lm} \int \bar{c}_{lm}^{(G)}(r) e^{i(\mathbf{G}_1 + \frac{1}{2}\mathbf{G}) \cdot \mathbf{r}} Y_{lm}(\hat{\mathbf{r}}) d\mathbf{r}$

We used the above expression to examine the relative stability of f.c.c and b.c.c structures under conditions of fluid-solid coexistence, as determined by MC simulations for soft spheres with $n=12, 6$ and 4 . In table 1 we give the values of ideal, symmetry conserving and

symmetry broken contributions to $\Delta W/N$. We note that the contribution arising due to symmetry broken part of DPCF is far from negligible and its importance increases with the softness of potential. While it is about one-fourth of the symmetry conserving part for $n=12$, for $n=4$ it increases to nearly one-half. As the contribution is negative it stabilizes the solid phase. Without it the theory strongly overestimates the stability of fluid phase specially for the softer repulsions ($n=6$ and 4) [11,20]. In agreement with simulation results we find that for $n=12$ the f.c.c structure on freezing is favored while for the softer repulsions ($n=6$ and 4), b.c.c structure is favored. From the values of $\Delta W/N$ given in the table we also conclude that while (3) is a good approximation for $c^{(b)}$ for $n \geq 12$ but it overestimates the value of $c^{(b)}$ as the softness of the repulsion increases. Because of this the crystal phase becomes stable at lower values of γ than found by simulations for $n = 6$ and 4 .

In conclusion, we developed a free-energy functional for a crystal that contains both symmetry conserved and symmetry broken parts of the direct pair correlation function. We calculated the symmetry conserving part of the pair correlation functions using the Ornstein-Zernike equation and the Roger-Young closure relation and used a perturbation expansion for $c^{(b)}$. The $c^{(b)}(\mathbf{r}_1, \mathbf{r}_2)$ has been expressed in the Fourier series in the center of mass variable with coefficient $c^{(G)}(\mathbf{r})$ which is function of difference $\mathbf{r} (= \mathbf{r}_1 - \mathbf{r}_2)$ and is found to differ considerably both in magnitude and in dependence on r for the b.c.c and f.c.c structures. In agreement with simulation results we find that for $n=12$ the freezing is into closed packed f.c.c structure while for soft repulsions ($n = 6$ and 4) b.c.c phase becomes more stable. The predictive power of the free-energy functional developed here can further be improved by improving the accuracy of $c^{(b)}(\mathbf{r}_1, \mathbf{r}_2)$ which can perhaps be achieved by including one more term in (3) [17].

We thank J. Ram and P. Mishra for their help in computation. This work was supported by a research grant from DST of govt. of India, New Delhi. One of us (SLS) thanks UGC (New Delhi) for research fellowship.

-
- [1] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).
 - [2] S. M. Stishov, Sov. phys. -Usp. **17**, 625 (1975).
 - [3] R. Agrawal and D. A. Kofke, Phys. Rev. Lett. **74**, 122 (1995).

- [4] B. B. Laird and A. D. J. Haymet, Mol. Phys. **75**, 71 (1992).
- [5] H. Ogura et. al. Progs. Theo. Phys. **58**, 419 (1992); W. G. Hoover et. al, J. Chem. Phys. **52**, 4931 (1970).
- [6] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B. **19**, 2775(1979).
- [7] Y. Singh, Phys. Rep. **207**, 351 (1991).
- [8] H. Lowen Phys. Rep. **237**, 249 (1994); J. Z. Wu, AIChE Journal **52**,1169 (2006).
- [9] J. L. Barrat, J. P. Hansen and G. Pastore, Mol. Phys. **63**, 747 (1988); Phys. Rev. Lett. **58**, 2075 (1987).
- [10] W. A. Curtin, J. Chem. Phys. **88**, 7050 (1988).
- [11] D. C. Wang and A. P. Gast, J. Chem. Phys. **110**, 2522 (1999).
- [12] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 4701 (1989); A. Khein and N. W. Ashcroft, Phys. Rev. Lett. **78**, 3346 (1997).
- [13] N. H. Phuong and F. Schmid, J. Chem. Phys. **119**, 1214 (2003).
- [14] P. Mishra and Y. Singh, Phys. Rev. Lett. **97**, 177801 (2006); P. Mishra et. al. J. Chem. Phys. **127**, 044905 (2007).
- [15] J. S. McCarley and N. W. Ashcroft, Phys. Rev. E **55**, 4990 (1997).
- [16] F. J. Rogers and D. A. Young, Phys. Rev. A **30**,999, (1984).
- [17] S. L. Singh and Y. Singh (to be published).
- [18] W. F. Saam and C. Ebner, Phys. Rev. A. **15**,2566 (1977).
- [19] P. Tarazona, Mol. Phys. **52**, 81 (1984).
- [20] J. L. Barrat et. al, J. Chem. Phys. **86**, 6360 (1987).

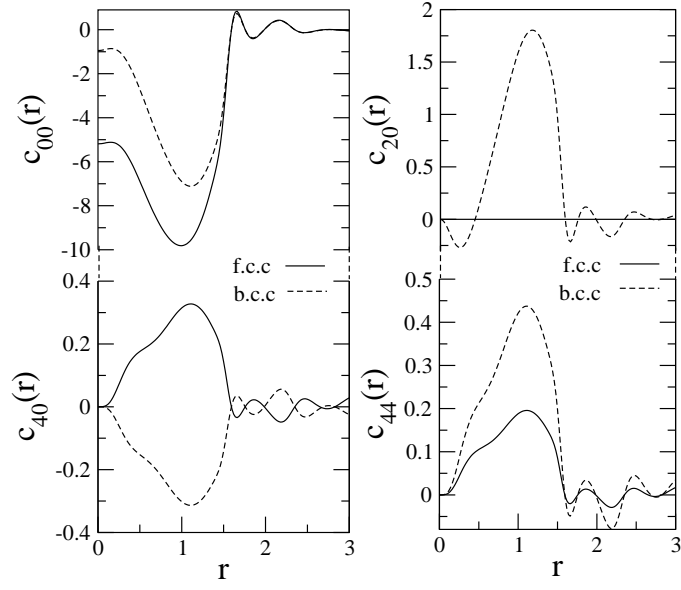


FIG. 1: Harmonic coefficients $c^{(G)}_{lm}(r)$ for a R. L. V. of the first set for $n = 12$.

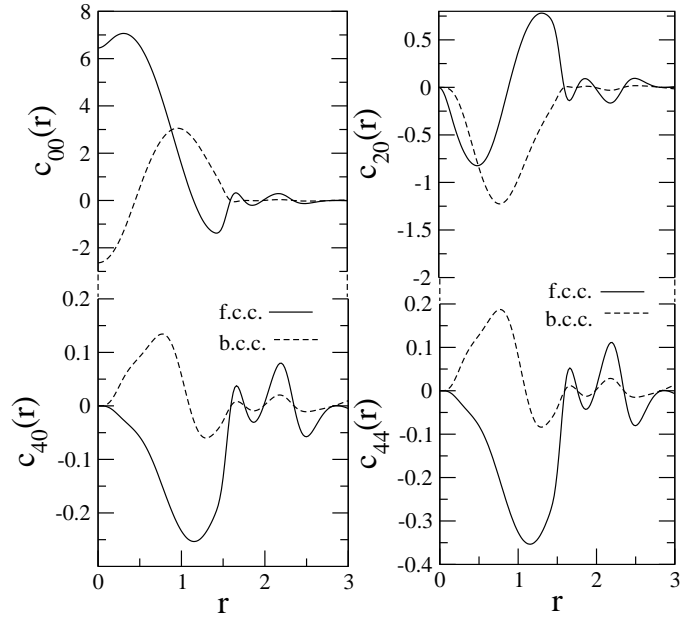


FIG. 2: Harmonic coefficients $c^{(G)}_{lm}(r)$ for a R. L. V. of the second set for $n = 12$.

TABLE I: Ideal ($\Delta W_{id}/N$), symmetry conserving ($\Delta W_0/N$) and symmetry broken ($\Delta W_b/N$) contributions to $\Delta W/N$ for f.c.c and b.c.c phases of three inverse power potentials ($n = 12, 6$ and 4) at fluid-solid coexistence. The coexistence parameters γ_s , γ_l , and L (the Lindemann parameter) are also given

| | structure | $\Delta W_{id}/N$ | $\Delta W_0/N$ | $\Delta W_b/N$ | $\Delta W/N$ |
|--|-----------|-------------------|----------------|----------------|--------------|
| $n = 12, L = 0.15$ $\gamma_s = 1.19, \gamma_l = 1.15$ | f.c.c | 2.80 | -2.29 | -0.50 | 0.01 |
| | b.c.c | 2.88 | -2.24 | -0.55 | 0.09 |
| $n = 6, L = 0.17$ $\gamma_s = 2.33, \gamma_l = 2.30$ | f.c.c | 2.38 | -1.80 | -0.62 | -0.04 |
| | b.c.c | 2.46 | -1.87 | -0.69 | -0.10 |
| $n = 4, L = 0.18$ $\gamma_s = 5.75, \gamma_l = 5.72$ | f.c.c | 2.19 | -1.60 | -0.72 | -0.13 |
| | b.c.c | 2.28 | -1.75 | -0.82 | -0.29 |